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## EUROPEAN PATENT APPLICATION

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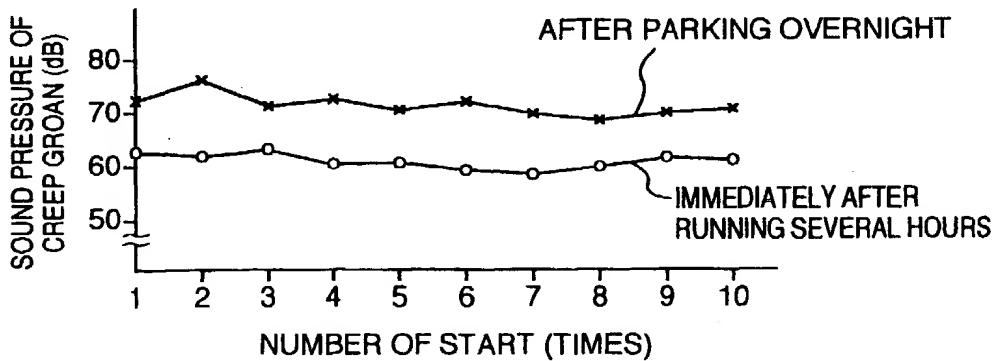
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### (54) Non-asbestos disc brake pad for automobiles

(57) A disc brake pad obtained by using a composition comprising a fibrous base material except for asbestos, a binder and a friction adjusting agent, wherein a silicone modified resin is contained as a part or whole

of the binder and zeolite is contained as a part of the friction adjusting agent can prevent a transfer film from contacting with water or remove the water once adsorbed in the transfer film and can lower the sound pressure of creep groan.

FIG.1



**Description****BACKGROUND OF THE INVENTION**

- 5 [0001] This invention relates to a non-asbestos disc brake pad for automobiles (hereinafter referred to as "disc brake pad").
- [0002] As a braking system for automobiles, there are used disc brakes, in which a disc brake pad is used as a braking part.
- [0003] Some known disc brake pads use asbestos (e.g. JP-A 49-21544, Junkatsu vol. 19, no. 9, p. 625-631 (1974)).
- 10 In contrast, JP-A 2-132175 discloses a non-asbestos friction material which is a mixture comprising a fibrous base material such as metal fibers, inorganic fibers and organic fibers; a binder including a thermosetting resin such as a phenol resin; and as a friction adjusting agent a lubricant such as graphite, antimony trisulfide, etc., a powder of metal such as iron, copper, brass, etc., a filler such as barium sulfate, calcium carbonate, etc. and/or an organic friction adjusting agent such as cashew dust, acrylonitrile-butadiene rubber (NBR), styrene-butadiene rubber (SBR), etc.. Such a mixture is subjected to molding with heating under pressure to give a disc brake pad.
- [0004] But automobiles using these prior art disc brake pads generate a noise which is so-called "creep groan". This noise seems to be derived from the generation of stick slip vibration when a creep torque of an automatic transmission is applied to a disc brake, said stick slip vibration being resonated to produce a noise. The frequency of this noise is usually about 200 to 300 Hz. When a car is driven again after parking the car for a long period of time, particularly after 20 parking (allowing to stand) the car overnight with a large change in temperature and/or humidity, the phenomenon of the creep groan occurs abruptly with a large amount at an initial stage of driving, which makes a driver uneasy and unpleasant.

**BRIEF SUMMARY OF THE INVENTION**

- 25 [0005] It is an object of the present invention to provide a disc brake pad capable of lowering a sound pressure of the creep groan by preventing a transfer film, which is obtained by attaching a part of the disc brake pad to oppositely placing disc rotor when braked, from water, or removing the water once adsorbed from the transfer film.
- [0006] The present invention provides a disc brake pad for automobiles obtained by using a composition comprising 30 a fibrous base material except for asbestos, a binder and a friction adjusting agent, wherein a silicone modified resin is contained as a part or whole of the binder, and zeolite is contained as a part of the friction adjusting agent.

**BRIEF DESCRIPTION OF THE DRAWINGS**

- 35 [0007] Fig. 1 is a graph showing a relationship between the number of start and the sound pressure of creep groan of a car equipped with a prior art disc brake pad after parking overnight and immediately after running several hours.
- [0008] Fig. 2 is a graph showing the results of measuring torque variation using a test piece of the prior art disc brake pad at a sliding surface of disc rotor adsorbing water after parking overnight.
- [0009] Fig. 3 is a graph showing the results of measuring torque variation using a test piece of the prior art disc brake 40 pad at a sliding surface of disc rotor adsorbing water immediately after running several hours.
- [0010] Fig. 4 is a graph showing a relationship between the number of start and the sound pressure of creep groan of cars equipped with the disc brake pads obtained in Example 1 and Comparative Examples 1 and 2 after parking overnight.

**45 DETAILED DESCRIPTION OF THE INVENTION**

- [0011] The present inventors have studied earnestly causes for generating creep groan of cars using prior art disc brake pads and found the following facts.
- [0012] A main cause for generating the creep groan seems to be that when a car is parked overnight, a transfer film 50 formed on a disc rotor surface adsorbs water, which generate rust between the disc rotor and the transfer film; and when the car is driven again, the transfer film is peeled off at the initial time of driving, resulting in increasing the noise level of the creep groan.
- [0013] Thus, the present inventors prepared disc brake pads from the friction material having a composition as shown in Table 1 and subjected to various tests.

Table 1

Material	Proportion (vol.%)
Phenol resin	20
Aramid fibers	10
Alumina - silica fibers	5
Potassium titanate fibers	15
Copper fibers	5
Graphite	3
Antimony trisulfide	2
Cashew dust	15
Isoprene rubber powder	5
Barium sulfate	20

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[0014] Fig. 1 is a graph showing a relationship between the number of start and the sound pressure of creep groan. More in detail, a car parking overnight, and a car immediately after running for several hours (i.e. after braking 200 times with a temperature before braking of 130°C, initial speed at braking of 60 km/hr, and brake deceleration of 0.3 G), respectively, are started slowly while relaxing a brake pedal, then stopped, and started slowly again while relaxing the brake pedal, and repeating this step 10 times, while measuring the sound pressure of creep groan generated at the time of relaxing the brake pedal using a sound-level meter.

[0015] As shown in Fig. 1, the car after parking overnight shows the highest sound pressure of 75 dB at the second start. On the other hand, the car immediately after running several hours shows the sound pressure of as low as 63 dB at the maximum sound pressure of creep groan.

[0016] The source of generation of the creep groan seems to be the stick slip vibration at the disc rotor sliding surface at the start of the vehicle. Then, the present inventors measured the torque variation (a difference between static coefficient of friction and dynamic coefficient of friction) using test pieces of disc brake pads at the sliding surface of a disc rotor adsorbing water after parking overnight, and at the sliding surface of a disc rotor immediately after running several hours. The results are shown in Figs. 2 and 3.

[0017] As is clear from Figs. 2 and 3, the disc rotor sliding surface of the car after parking overnight becomes to have a larger torque variation due to adsorption of water, resulting in generating the stick slip vibration. Further, on the sliding surface of disc rotor of the car after parking overnight and adsorbing water, a large number of fine rust was observed. In contrast, the disc rotor sliding surface of the car immediately after running several hours showed a little torque variation.

[0018] After studying earnestly taking the results mentioned above into consideration, the present inventors found that in order to prevent the transfer film from adsorbing water or to remove the water once adsorbed in the transfer film, it was effective to use a silicone modified resin as a part or whole of the binder and zeolite as a part of the friction adjusting agent. By doing this, it was possible to provide a disc brake pad capable of lowering the sound pressure of creep groan. Thus, the present invention has been accomplished.

[0019] The disc brake pad for automobiles of the present invention is obtained by using a composition comprising a fibrous base material except for asbestos, a binder and a friction adjusting agent, wherein a silicone modified resin is contained as a part or whole of the binder, and zeolite is contained as a part of the friction adjusting agent.

[0020] In the disc brake pad of the present invention, when the silicone modified resin is contained in the composition in an amount of 3 to 30% by volume, the resulting disc brake pad is excellent in thermal fade phenomenon.

[0021] When the silicone modified resin is obtained by reacting silicone oil or silicone rubber with a novolak phenol resin, or obtained by finely dispersing silicone oil or silicone rubber in a novolak phenol resin, moldability of the disc brake pad is further improved.

[0022] Further, when zeolite having a moisture absorption rate of 5% or more is used, the resulting disc brake pad is improved in removing the water once adsorbed.

[0023] In addition, when zeolite is contained in the composition in an amount of 0.5 to 20% by volume, the resulting disc brake pad is remarkably effective for preventing the generation of brake noise such as so-called brake squeal with about 2000 to 10,000 Hz.

[0024] Moreover, when zeolite having an average particle size of 1 to 50 µm is used in the composition, the resulting disc brake pad is improved in removing the water once adsorbed.

[0025] In the present invention, conventional binders can be used and there is no particular limitation thereto. But, by using the silicone modified resin as a part or whole of the binder, water repellency is by far preferably improved. As the silicone modified resin, it is preferable to use a resin obtained by reacting silicone oil or silicone rubber with a

novolak phenol resin, or a resin obtained by finely dispersing silicone oil or silicone rubber in a novolak phenol resin. The amount of the silicone modified resin in the composition is in an amount of preferably 3 to 30% by volume, more preferably 10 to 25% by volume.

**[0026]** In order to react the silicone oil or silicone rubber with the novolak phenol resin, it is sufficient to add silicone oil or silicone rubber to heated novolak phenol resin and to mix well so as to react each other according to a conventional method. Further, in order to finely disperse the silicone oil or silicone rubber in the novolak phenol resin, it is sufficient to add the silicone oil or silicone rubber to the novolak phenol resin, followed by stirring the mixture so as not to react each other, or even if reacted in a very slight amount.

**[0027]** As a part of the friction adjusting agent, zeolite should be used in the present invention in order to improve water removing properties. As the zeolite, either synthetic or natural zeolite can be used. The water absorption rate of the zeolite is preferably 5% or more, more preferably 12% or more.

**[0028]** The water absorption rate of the zeolite is obtained as follows. Zeolite heat treated at 600°C for 1 hour is allowed to stand under standard conditions (at 21°C and a relative humidity of 65%) until the temperature of the zeolite becomes 50°C or less, followed by measurement of the weight (A) simultaneously. After measuring, the zeolite is allowed to stand at 50°C and a relative humidity of 90% for 6 hours, followed by measurement of the weight (B). The water absorption rate is obtained from the following equation:

$$\text{Water absorption rate (\%)} = [(B) - (A)]/(A) \times 100$$

**[0029]** The amount of the zeolite in the composition is preferably 0.5 to 20% by volume, more preferably 2 to 10% by volume.

**[0030]** There is no particular limit to the shape of zeolite, but it is preferable to have an average particle size of 1 to 50 µm, more preferably 1 to 10 µm.

**[0031]** As the fibrous base material, there can be used any fibers except for asbestos. Examples of the fibrous base material are organic fibers such as aramide fibers, acrylic fibers, phenol fibers, etc.; inorganic fibers such as glass fibers, ceramic fibers, rock wool, potassium titanate fibers, etc.; and metal fibers such as steel fibers, copper fibers, brass fibers, bronze fibers, etc. These fibers can be used alone or as a mixture thereof.

**[0032]** The amount of the fibrous base material in the composition is preferably 20 to 50% by volume, more preferably 25 to 45% by volume.

**[0033]** As the binder, there can be used a polyimide resin, a furan resin, etc. in addition to the silicone modified resin. The amount of the additional binder component in the composition is 10 to 30% by volume, more preferably 15 to 25% by volume.

**[0034]** As the friction adjusting agent, there can be used, in addition to the zeolite, inorganic friction adjusting agents such as graphite, antimony trisulfide, molybdenum disulfide, barium sulfate, potassium carbonate, magnesium carbonate, etc.; organic friction adjusting agents such as cathew dust, acrylic rubber, isoprene rubber, NBR, SBR, etc.; metal powders such as iron powder, brass powder, tin powder, zinc powder, etc.; and grinding materials such as mica, alumina, silica, zircon, mullite, talc, clay, etc. These friction adjusting agents can be used alone or as a mixture thereof.

**[0035]** Total amount of the friction adjusting agents in the composition is preferably 20 to 70% by volume, more preferably 35 to 55% by volume.

**[0036]** The components mentioned above are blended so as to make the total composition 100% by volume.

**[0037]** In the present invention, the percent by volume of each component is obtained by dividing the weight of the component by the density of the component.

**[0038]** The disc brake pad of the present invention can be obtained by uniformly mixing the composition comprising a fibrous base material except for asbestos (preferably 20 to 50% by volume), a binder (preferably 10 to 30% by volume), and a friction adjusting agent (preferably 20 to 70% by volume), a total being 100% by volume, preforming the mixed composition, inserting a back metal and the preformed composition into a mold, molding under pressure with heating, and heat treating the molded article. The heating temperature at the molding is preferably 130 to 170°C, more preferably 140 to 160°C. The pressure at the molding is preferably 20 to 60 MPa, more preferably 30 to 50 MPa.

**[0039]** The temperature at the heat treatment is preferably 100 to 300°C, more preferably 150 to 250°C.

**[0039]** The present invention is illustrated by way of the following Examples.

#### Example 1, Comparative Example 1

**[0040]** Components shown in Table 2 were mixed uniformly in a mixer, followed by preform. Each preformed composition was placed in a mold together with a back metal and molded at 140°C under a pressure of 40 MPa for 10 minutes, followed by heat treatment at 200°C for 6 hours to give a disc brake pad. In Table 2, as the silicone modified resin, a resin obtained by reaction silicone rubber with novolak phenol resin (RS 2210MB, a trade name, mfd. by Mitsui

Chemicals, Inc.) was used. As the zeolite, synthetic zeolite having a water (moisture) absorption rate of 9% and an average particle size of 2 µm was used.

Table 2

		Example 1	Comparative Example 1
5	Binder	Silicone modified resin	20
10	Fibrous base material	Aramid fibers*1	10
		Alumina Silica fibers	5
		Potassium titanate fibers	15
		Copper fibers	5
15	Friction adjust-agent	Graphite*2	3
		Antimony trisulfide	2
		Cashew dust	15
		Isoprene rubber powders	5
		Barium sulfate	15
		Zeolite	5
20	(Note)		

\*1: Kevlar fibers mfd. by DuPont-Toray Co., Ltd.

\*2: CB 150, trade name, mfd. by Nippon Graphite Industries, Ltd.

[0041] The disc brake pad of Example 1 and that of Comparative Example 1 were built in each car and subjected to a test for measuring a sound level of creep groan after parking (standing) overnight. The creep groan was evaluated by starting each car slowly while relaxing the brake pedal, stopping the car, and then starting the car again slowly while relaxing the brake pedal, repeating this step 10 times, while measuring the sound pressure of creep groan generated at the time of relaxing the brake pedal using a sound-level meter.

[0042] As a result, the disc brake pad of Example 1 showed as low as 68 dB at maximum, while the disc brake pad of Comparative Example 1 showed as high as 72 dB at maximum.

[0043] Then, the torque variation of a test piece of the disc brake pad of Example 1 at a disc rotor sliding surface adsorbing water after parking overnight was measured and compared with that of Comparative Example 1.

[0044] As a result, the torque variation at the disc rotor sliding surface using the disc brake pad of Example 1 was as small as 23 Nm, while the torque variation of the disc brake pad of Comparative Example 1 was as high as 35 Nm.

### 35 Comparative Example 2

[0045] A disc brake pad was produced in the same manner as described in Example 1 using the composition as shown in Table 3.

Table 3

Material	Proportion (vol.%)
Phenol resin	20
Aramid fibers	10
Alumina - silica fibers	5
Potassium titanate fibers	15
Copper fibers	5
Graphite	3
Antimony trisulfide	2
Cashew dust	15
Isoprene rubber powder	5
Barium sulfate	15
Zeolite	5

[0046] The resulting disc brake pad was built in a car and subjected to measurement of the sound pressure of creep groan in the same manner as described in Example 1. Further, the torque variation of the disc brake pad at the disc

5 rotor sliding surface adsorbing water after parking overnight was as large as 35 Nm.

10 [0047] The data (10 times) of sound pressure of creep groan of the disc brake pads of Example 1, Comparative Example 1 and Comparative Example 2 are shown in Table 4.

Table 4

	Example 1	Comparative Example 1	Comparative Example 2
10 15 20	67	71	72
	68	72	71
	68	72	72
	68	72	71
	68	72	71
	67	71	69
	67	71	69
	66	70	69
	66	69	68
	66	69	68
25	Maximum (dB)	68	72

[0048] The results of Table 4 are shown in Fig. 4.

[0049] As is clear from Fig. 4, the disc brake pad of the present invention is improved so as to lower the sound pressure of creep groan and make the torque variation small.

[0050] As mentioned above, the disc brake pad of the present invention obtained from the composition wherein the silicone modified resin is used as a part or whole of the binder, and zeolite is used as a part of the friction adjusting agent, is effective for preventing the transfer film from contacting with water, or for removing the water once adsorbed in the transfer film so as to lower the sound pressure of creep groan. Thus, the disc brake pad of the present invention is very suitable for use industrially.

[0051] Further, the disc brake pad of the present invention obtained from the composition containing 3 to 30% by volume of silicone modified resin is excellent in thermal fade phenomenon in addition to the above-mentioned features.

[0052] In addition, the disc brake pad of the present invention obtained from the composition wherein as the silicone modified resin a resin obtained by reacting silicone oil or silicone rubber with a novolak phenol resin, or obtained by finely dispersing silicone oil or silicone rubber in a novolak phenol resin, shows the features mentioned above with excellent molding properties.

[0053] Moreover, the disc brake pad of the present invention obtained from the composition containing zeolite having a water (moisture) absorption rate of 5% or more is excellent in removing water in addition to the features mentioned above.

[0054] The disc brake pad of the present invention obtained from the composition containing 0.5 to 20% by volume of zeolite is remarkably effective for preventing the generation of brake noise such as so-called brake squeal of about 2000 to 10,000 Hz in addition to the features mentioned above.

[0055] The disc brake pad of the present invention obtained from the composition containing zeolite having an average particle size of 1 to 50 µm is excellent in removing water in addition to the features mentioned above.

#### 45 Claims

1. A disc brake pad for automobiles obtained by using a composition comprising a fibrous base material other than asbestos, a binder and a friction adjusting agent; wherein the binder comprises a silicone modified resin, and the friction adjusting agent comprises a zeolite.
2. A disc brake pad according to claim 1, wherein the silicone modified resin is contained in an amount of 3 to 30% by volume in the total composition.
3. A disc brake pad according to claim 1 or 2, wherein the silicone modified resin is obtainable by reacting silicone oil and/or silicone rubber with a novolak phenol resin.
4. A disc brake pad according to claim 1 or 2, wherein the silicone modified resin is obtainable by finely dispersing

**EP 0 959 262 A1**

silicone oil and/or silicone rubber in a novolak phenol resin.

5. A disc brake pad according to any preceding claim, wherein the zeolite has a moisture absorption rate (as herein defined) of 5%, or more.
6. A disc brake pad according to any preceding claim, wherein the zeolite is contained in an amount of 0.5 to 20% by volume in the total composition.
7. A disc brake pad according to any preceding claim, wherein the zeolite has an average particle size of 1 to 50 µm.

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FIG.1

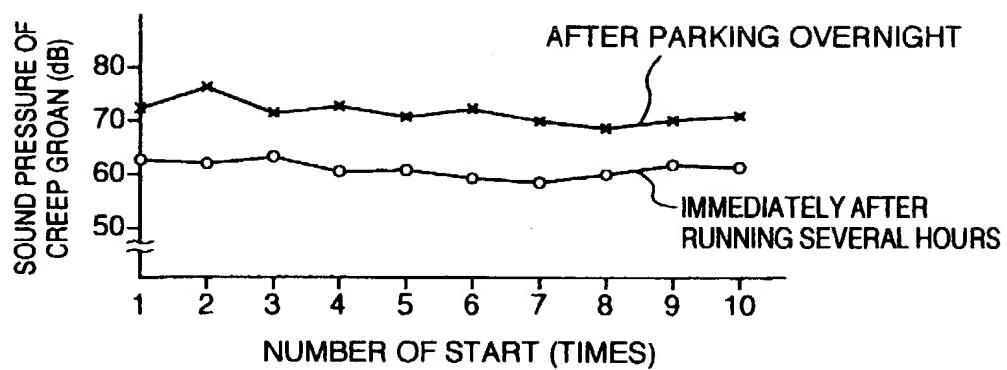


FIG.2

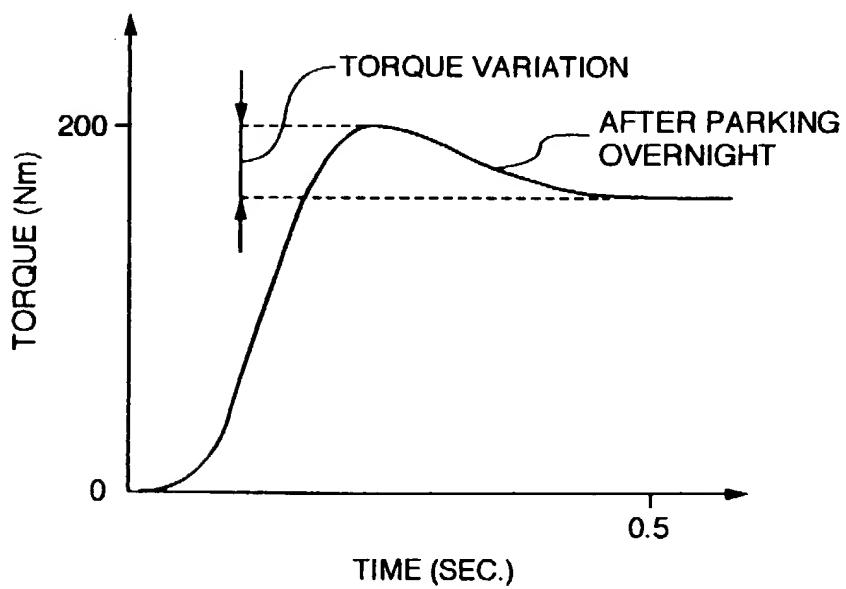


FIG.3

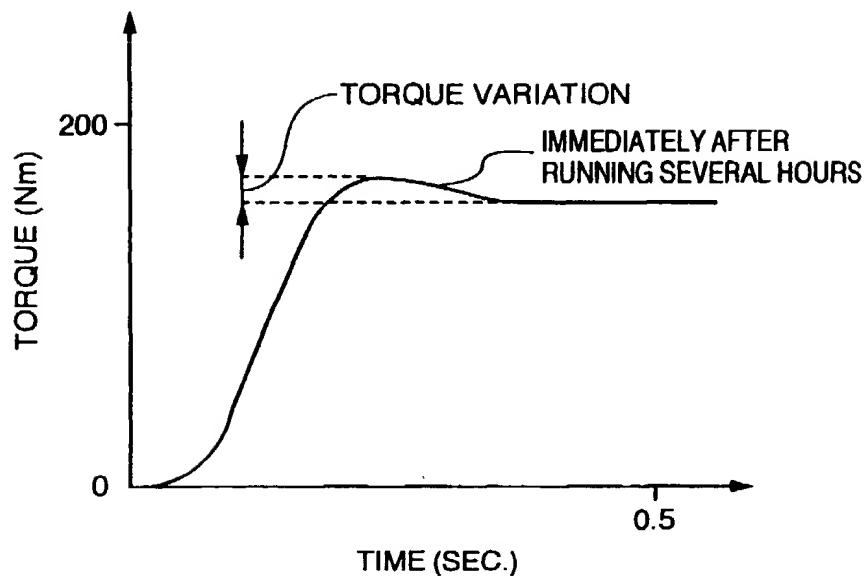
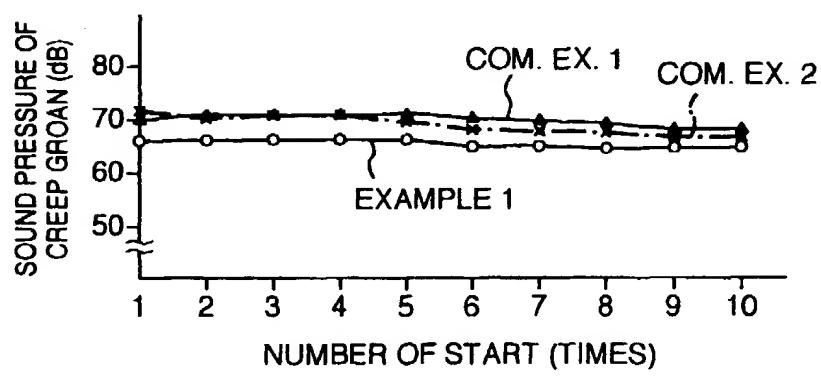


FIG.4





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## EUROPEAN SEARCH REPORT

Application Number  
EP 99 30 3875

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
Y	<p><b>DATABASE WPI</b>  <b>Section Ch, Week 9807</b>  <b>Derwent Publications Ltd., London, GB;</b>  <b>Class A12, AN 98-075487</b>  <b>XP002110754</b>  <b>&amp; RU 2 081 133 C (VASILEV YU N)</b>  <math>\text{, 10 June 1997}</math>  <b>* abstract *</b>  <math>\text{---}</math></p>	1-4,6	F16D69/02
Y	<p><b>DATABASE WPI</b>  <b>Section Ch, Week 8931</b>  <b>Derwent Publications Ltd., London, GB;</b>  <b>Class A81, AN 89-223260</b>  <b>XP002110755</b>  <b>&amp; JP 01 158238 A (HITACHI CHEM CO LTD)</b>  <math>\text{, 21 June 1989}</math>  <b>* abstract *</b>  <math>\text{---}</math></p>	1-4,6	
Y	<p><b>US 5 563 196 A (S.KITAHARA)</b> 8 October 1996  <b>* column 3, line 16 - line 39 *</b>  <b>* column 4, line 26 - line 31 *</b>  <math>\text{---}</math></p>	1-4	
Y	<p><b>DATABASE WPI</b>  <b>Section Ch, Week 9807</b>  <b>Derwent Publications Ltd., London, GB;</b>  <b>Class A60, AN 98-075484</b>  <b>XP002110756</b>  <b>&amp; RU 2 081 129 C (VASILEV YU N)</b>  <math>\text{, 10 June 1997}</math>  <b>* abstract *</b>  <math>\text{---}</math></p>	1-4	F16D
Y	<p><b>EP 0 807 766 A (BORG-WARNER)</b>  <b>19 November 1997</b>  <b>* page 3, line 10 - line 18 *</b>  <b>* page 4, line 38 - line 41 *</b>  <b>* page 6, line 22 - line 49 *</b>  <b>* page 27, line 40 - line 45 *</b>  <math>\text{---}</math></p>	1-4	
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	29 July 1999	Boulon, A	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 3875

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
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29-07-1999

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